11-7-2017

Gold Polar Intermetallics: Structural Versatility through Exclusive Bonding Motifs

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Abstract
The design of new materials with desired chemical and physical characteristics requires thorough understanding of the underlying composition–structure–property relationships and the experimental possibility of their modification through the controlled involvement of new components. From this point of view, intermetallic phases, a class of compounds formed by two or more metals, present an endless field of combinations that produce several chemical compound classes ranging from simple alloys to true ionic compounds. Polar intermetallics (PICs) belong to the class that is electronically situated in the middle, between Hume–Rothery phases and Zintl compounds and possessing e/a (valence electron per atom) values around 2. In contrast to the latter, where logical rules of formation and classification systems were developed decades ago, polar intermetallics remain a dark horse with a huge diversity of crystal structures but unclear mechanisms of their formation. Partial incorporation of structural and bonding features from both nonpolar and Zintl compounds is commonly observed here. A decent number of PICs can be described in terms of complex metallic alloys (CMAs) following the Hume–Rothery electron-counting schemes but exhibit electronic structure changes that cannot be explained by the latter. Our research is aimed at the discovery and synthesis of new polar intermetallic compounds, their structural characterization, and investigation of their properties in line with the analysis of the principles connecting all of these components. Understanding of the basic structural tendencies is one of the most anticipated outcomes of this analysis, and systematization of the available knowledge is the initial and most important step.

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Gold Polar Intermetallics: Structural Versatility through Exclusive Bonding Motifs

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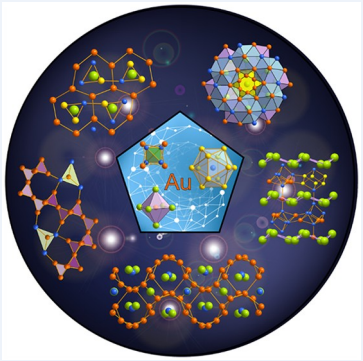
Supporting Information

CONSPECTUS: The design of new materials with desired chemical and physical characteristics requires thorough understanding of the underlying composition−structure−property relationships and the experimental possibility of their modification through the controlled involvement of new components. From this point of view, intermetallic phases, a class of compounds formed by two or more metals, present an endless field of combinations that produce several chemical compound classes ranging from simple alloys to true ionic compounds. Polar intermetallics (PICs) belong to the class that is electronically situated in the middle, between Hume−Rothery phases and Zintl compounds and possessing e/a (valence electron per atom) values around 2. In contrast to the latter, where logical rules of formation and classification systems were developed decades ago, polar intermetallics remain a dark horse with a huge diversity of crystal structures but unclear mechanisms of their formation. Partial incorporation of structural and bonding features from both nonpolar and Zintl compounds is commonly observed here. A decent number of PICs can be described in terms of complex metallic alloys (CMAs) following the Hume−Rothery electron-counting schemes but exhibit electronic structure changes that cannot be explained by the latter. Our research is aimed at the discovery and synthesis of new polar intermetallic compounds, their structural characterization, and investigation of their properties in line with the analysis of the principles connecting all of these components. Understanding of the basic structural tendencies is one of the most anticipated outcomes of this analysis, and systematization of the available knowledge is the initial and most important step.



In this Account, we focus on a well-represented but rather small section of PICs: ternary intermetallic compounds of gold with electropositive and post-transition metals of groups 12 to 15. The strong influence of relativistic effects in its chemical bonding results in special, frequently unique structural motifs, while at the same time gold participates in common structure types as an ordinary transition element. Enhanced bonding strength leads to the formation and stabilization of complex homo- and heteroatomic clusters and networks that are compositionally restricted to just a few options throughout the periodic table. Because it has the highest absolute electronegativity among metals, comparable to those of some halogens, gold usually plays the role of an anion, even being able to form true salts with the most electropositive metals. We discuss the occurrence of the structure types and show the place of gold intermetallics in the general picture. Among the structures considered are ones as common as AlB_2 or $BaAl_4$ types, in line with the recently discovered diamond-like homoatomic metal networks, formation of local fivefold symmetry, different types of tunneled structures, and more complex intergrown multicomponent structures.

1. INTRODUCTION

Relativistic effects have a considerable influence on the chemical and physical properties of the heavier elements and their compounds.[1−3] Since the relativistic orbital contraction affects mostly the s states, this is especially important for Au and Pt, which also exhibit a special shell structure ($5d^m6s^n$). One of the most extreme outcomes of this combination is the formation of saltlike compounds with cesium: CsAu, Cs_2Pt, Cs_3AuO, and Cs_9Pt_4H.[4−9] Following the tendency, the presence of Au in combination with some active and post-transition metals revealed its unique role in the stabilization of certain structure types known mainly for pnictides (Pn), where gold almost exclusively plays the role of the latter, i.e.,

$_9Au_5-BaNi_9As_5$,[10] $Ae_2Au_3In_4-Hf_2Co_4P_3$,[11] and $AAu_4In_6-LiCo_6P_4$ (Ae = alkaline-earth metal, A = alkali metal).[12] On the other hand, Au was found to influence some active metals, leading to stable phases that otherwise were predicted to not exist: i-$Na_{13}Au_{12}Ga_{15}$.[13] Strong Au−Au bonds due to relativistically destabilized d orbitals lead to a big number of Au-rich phases and a variety of homoatomic formations within them, ranging from separated clusters to three-dimensional (3D) networks. The compounds with lower Au content tend to stabilize through the maximization of heteroatomic contacts, particularly through mixed positions of the latter with p elements.[14] All of these features together allow for augmentation of intermetallics with a wide variability of unique or uncommon structure types and often useful physical and chemical properties such as catalysis, superconductivity, the magnetocaloric effect, thermoelectricity, and ferromagnetism.[14−18]

It is worth noting that within the 118 elements discovered to date, the majority are metals forming a few hundred thousand reported intermetallic compounds.[19] Several systems have been historically developed for proper ordering and classification of the existing compounds, while rare attempts have been made to establish relationships among the latter. Among them we outline the work of Krypiakevych[20] with classification based on coordination polyhedra and partially their orientation, accounting for both chemical and geometric aspects of the structure formation. The most recent work proposes symmetry-based analysis in terms of group−subgroup relations (the Bärnighausen formalism).[21]

In this Account, we present a full picture of exploratory results combined with an analysis of structural and electronic features with rather limited relation to their symmetries. Complemented with the usual analysis by symmetry or investigation of local environments by means of coordination numbers, we consider mainly larger structural motifs as result of mutual arrangement of primitive building blocks. Analysis by structural fragments combines the advantages of the chemical and symmetrical approaches, reveals similarities between symmetrically unrelated formations, and opens wider horizons for an understanding of the structural relationships.

2. STRUCTURES WITH LOCAL (PSEUDO) FIVEFOLD SYMMETRY

Quasicrystals (QCs) exhibit crystallographically forbidden rotational symmetries and aperiodic long-range positional order. While in certain cases periodic and quasiperiodic lattices may coexist (structures with 1D and 2D quasiperiodicity), Au-containing QCs are known only for three groups of 3D quasiperiodic lattices containing Bergman (B), Tsai (T), and Mackay (M) type clusters and are limited to 14 reported representatives (Table S1). The role of Au in each of these types is different: an electron-tuning agent in the T type, a rather stabilizing impurity in the M type, and an irreplaceable component in the B type. Most of these compounds are thermodynamically unstable, except for three specimens with trivalent cations and one with sodium. The unique representative of the Bergman type is known in the Na−Au−Ga system, whereas the Mackay type is represented by a few Zr-based solid solutions. Though the valence electron counting (*vec*) for the transition metals is still controversial, the Mackay type is claimed to exist with $1.6 \le e/a \le 1.9$, where e/a is the number of valence electrons per atom. Recent explorations in the systems with Au and some active metals revealed somewhat wider stability ranges for Bergman and Tsai types ($1.75 \le e/a \le 2.2$).[22]

In contrast to the quasicrystalline phases, QC approximants (ACs) and their isostructural analogues are better represented and characterized (Table S2). All known i-QC approximant types can be divided into three main groups on the basis of their structural proximity to the QC building blocks using the corresponding numbers of the Fibonacci row: 1/0, 1/1, and 2/1.[23] The 1/0 approximants are identical for all types and appear to be strongly electronically restricted, revealing an e/a ratio of strictly 1.6. At the 1/1 stage, the difference between the Bergman and Tsai clusters becomes evident. The Bergman type represents a usually better organized case with a reasonable presence of occupational disorder, while the Tsai type involves both occupational and positional disorder as well as their combination. Both types can be described in terms of five-shell multiply endohedral clusters.[22] Similar to the QC phases, Au-containing Bergman-type 1/1 and 2/1 ACs exist only with sodium and a series of triels/tetrels, while the Tsai type is represented by the majority of rare-earth metals and calcium. Because of the different occupations of the cluster centers, the cation/anion ratios deviate from the classical 1:6 (YCd_6 type) and range from 1:5.2 to 1:6.3. The higher-order Tsai-type ACs with gold were observed only with divalent cations (Ca, Eu, and Yb). This means that *vec* is an important factor, but the size and nature of the formally electropositive constituent plays a more important role in the structural preference, although the role of Au is essential in the total bonding, especially with the least electronegative metals Na and Ca.

Beside QCs and ACs, the systems with Au, triels, and light alkali metals (mostly Na) contain compounds exhibiting structural components with local fivefold symmetry□icosahedra and polyicosahedral clusters, pentagonal bipyramids, and prisms (Table S3). Multiply endohedral clusters observed in $K_{34}Au_9In_{96}$, $Na_{17}Au_6Ga_{47}$, and $Na_{1.0}Au_{0.2}Ga_{1.8}$ ideally follow the first three shells of the classical Bergman-type sequence. The next shell, the M_{60} buckyball-like polyhedron, surprisingly allows inclusion of the formal cation, Na. The fifth shell may already be missing or even more considerably distorted because of the combination of anionic and cationic groups (Figure 1).

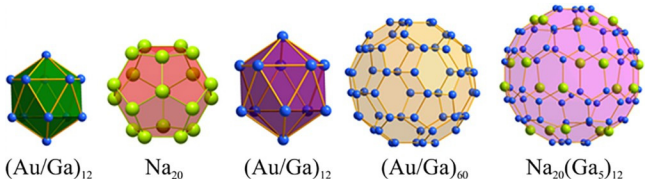


Figure 1. Modified Bergman-type clusters in the crystal structure of $Na_{17}Au_6Ga_{47}$.

$Na_{128}Au_{81}Ga_{275}$, an extremely complex, unique structure type, contains both 3D and 2D pseudo-fivefold elements (icosahedra, dodecahedra, and their fragments) and is rather a transition variant between icosahedral and decagonal approximants. Solely 2D pentagonal fragments, i.e., pentagonal bipyramids or prisms (Figure 2), have been observed in the two closely related orthorhombic compounds $Na_8Au_{10}Ga_7$ and $Na_8Au_{11}In_6$, which are possible candidates for decagonal ACs.

3. TUNNEL STRUCTURES

Compounds with planar or puckered layers whose mutual (dis)location leads to the formation of tunnels in the direction

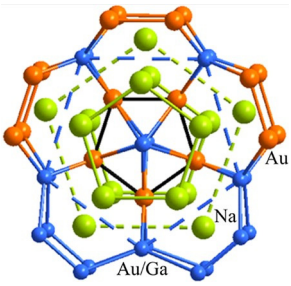


Figure 2. Pseudo-fivefold fragments in the crystal structure of $Na_8Au_{10}Ga_7$.

orthogonal to the latter represent perhaps the most common structural motif in intermetallic compounds. Some of the structure types have been known for long time (e.g., AlB_2 and $BaAl_4$), contain many derivatives, and are well-characterized, while others are element-restricted, contain a limited number of members, or have not been deeply investigated. Here we focus on the new representatives, the distribution of Au within the known types, and its role in their existence.

3.1. Hexagonal Diamond Networks

A diverse group of compounds with the structural motifs of the hexagonal diamond (lonsdaleite) has been discovered in the Au-richer regions of the systems with divalent cations and a majority of post-transition metals (Table S4). While the possibility of a metallic network with the structure of lonsdaleite was uncovered with Ag decades ago,[24] such compounds with Au, especially those containing homoatomic metal nets, remained unknown until recently. All of the compounds in the series represent 3D honeycomb networks (Figure 3) with different degrees of distortion, and all of the voids are filled either by an active metal or anionic T_3 associates, represented mostly by metals of group 13−15 with or without Au intercalation. The general composition of the series is best described as $(Ae@Au_{12/6})_m(T_3@Au_{12/6})_n = (AeAu_2)_m(T_3Au_2)_n$, where the Ae subseries with Sr, Ba, and Eu follows the mn sequence of the Fibonacci row.[25]

It is interesting that the Ae/T_3 ratio never drops below 1, indicating an important role of the formal electron donors for the network stabilization, although higher Ae/T_3 ratios always lead to a certain degree of mixing involving the Au diamond network, which is also the case for the unique Ag representative. On the basis of the up-to-date experimental evidence, the formation of homoatomic diamond networks is a unique feature of gold that is apparently due to strong relativistic effects in its bonding. On the other hand, "stabilizing impurities" are required to observe certain modifications of that structural motif. Because of the high Au proportions, the compounds exhibit rather low e/a ratios ranging from 1.27 to 1.88, hence covering the upper range of the Hume−Rothery phases. This overlap is also reflected in a series of structural aspects including not only anionic substitutions but also the possibility of partial cation/anion exchange, as observed in the systems with barium and europium.

3.2. Uniform Anionic Tunnels with Linearly Distributed Cations

All of the compounds in this family can be assigned to a few groups on the basis of the (pseudo)symmetry of the tunnels (or more accurately their projections) and the structures of the single layers forming them. The relatively new tetragonal group is based on the KPt_4Si_4 type,[26] while the hexagonal group is limited to the well-known AlB_2 type with a decent number of its derivatives (Table S5). The first group exhibits tunnels formed by eight-membered rings that are connected to each other through additional empty rhombi, whereas the latter contains regular or distorted honeycombs (Figure 4).

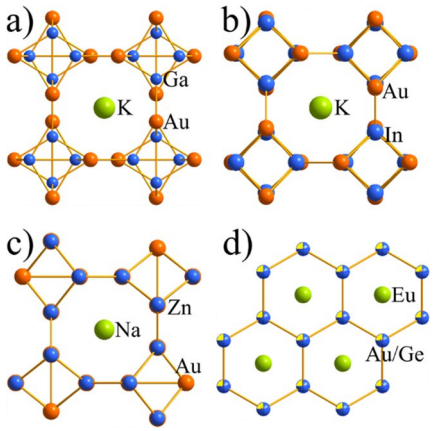


Figure 4. Projections of the crystal structures of (a) $K_{0.56}Au_2Ga_2$, (b) $K_{1.76}Au_6In_4$, (c) $NaAu_2Zn_4$, and (d) Eu(Au,Ge) as representative cases for uniform pseudo-octagonal and hexagonal tunnels.

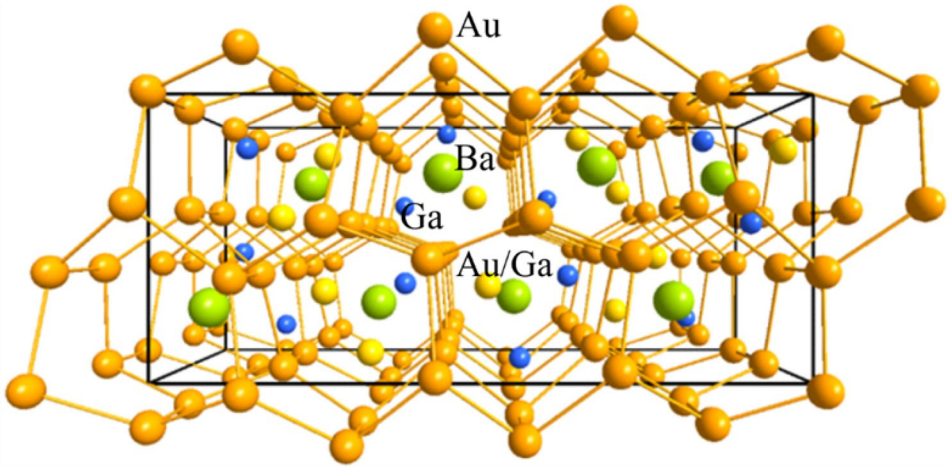


Figure 3. Au lonsdaleite network with filled honeycombs in the crystal structure of $BaAu_5Ga_2$.

A detailed overview of the AlB_2 type and its derivatives based on symmetry relations was given in a recent publication.[27] This type is very common throughout the periodic table, so we just summarize the available Au representatives. A uniform distribution of cations in the tunnels is observed in both the hexagonal and orthorhombic branches of this group and does not directly depend on the structure of a single anionic layer (planar or puckered). The tetragonal family instead requires participation of at least one late transition element that includes group 10 or Au, with the latter being the most represented. Because of the relatively large tunnel diameter, the main characteristic feature of the tetragonal family is the presence of a rather huge cationic disorder. This disorder depends on the cation's nature and varies for different gold to post-transition metal proportions and changes from the preferred site occupation for the light alkali metals to a nonstatistical distribution for the heavier ones.[28] The lowest-symmetry and most cation-rich member of this group, Na_4AuTl, comes rather as an exception revealing cationic tunnels with encapsulated anions. R_5Au_2E, the unique non-alkali representative, contains identical structural motifs combined with total sharing of the cation/anion roles.

3.3. Variable Anionic Tunnels with Linearly Distributed Cations

A big group of compounds can be characterized on the basis of cation-centered polyhedra consisting of parallel (planar or slightly puckered) membered rings sharing the biggest faces along a certain direction (Table S6). In contrast to the previous family, the number of atoms in each ring varies, leading to a sinusoid-like shape of the tunnel walls along the same direction and a much better separation of cation positions. The most common arrangements are represented in Figure 5. The

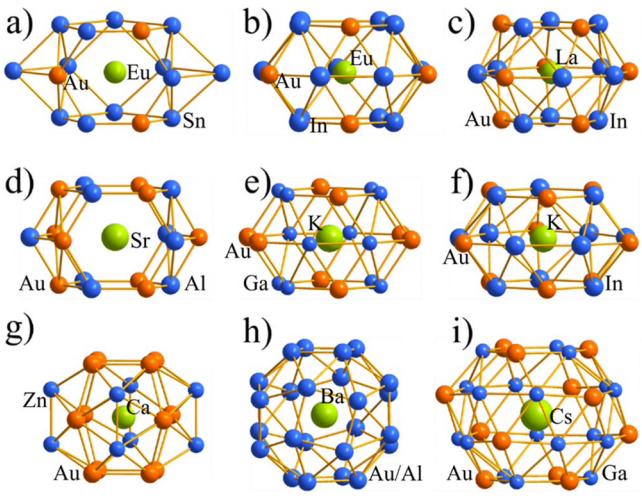


Figure 5. Basic building units in the crystal structures of (a) $Eu_2Au_2Sn_5$, (b) $EuAuIn_4$, (c) $LaAu_2In_4$, (d) $SrAu_2Al_2$, (e) KAu_2Ga_4, (f) KAu_4In_6, (g) $CaAu_4Zn_2$, (h) $BaAu_6Al_6$, and (i) $CsAu_5Ga_9$.

complexity of some of these structures leads to the presence of two or more distinct building units that share faces. A general occupation of the membered ring is provided in Table S6. The classical example is the $BaAl_4$ type and its derivatives. The appearance of an extra cation position in the coordination sphere leads to larger nontrigonal faces shared with the neighboring tunnels and a significant polyhedron distortion. Though the cation−cation separations are considerably shorter than the sum of their atomic radii, they are well-isolated, and no positional disorder is possible. On the other hand, the large size of some cations (i.e., Rb^+, Cs^+, or Ba^{2+}) may lead in some cases to disorder in the polyanionic network.

All of the compounds in this family can be grouped by the number of atoms in the capping rings or by the total number of rings. Small cations are surrounded, as a rule, by three rings and larger ones (Rb, Ba, and Cs) by four. An intermediate option is the $YbMo_2Al_4$ type, which formally has five rings but in a very dense packing. The $Ca@Au_{12}Zn_8$ polyhedron of this type is comparable to $K@Au_8Ga_{12}$ in KAu_2Ga_4 but definitely smaller than any of the $NaZn_{13}$ type having just four parallel slightly puckered rings. Another single exception is observed in KAu_4Sn_6, which has rather typical and regular 6/8/6 units that are separated from each other by Sn_2 pairs in the second coordination sphere of K, so the tunnel shape can best be descibed as 2/6/8/6/2. The largest cation is unique for the $Cs@Au_{12}Ga_{18}$ polyhedron, with 30 atoms distributed within four levels. With no dependence on size and anion/cation proportion in a compound, the central ring is never populated by more than nine members, including extra neighbors of the same type shared with the neighboring units.

This family also contains some common and well-described types, i.e., $BaAl_4$ and $NaZn_{13}$ and branchy trees of their derivatives.[14,29] While being represented in the parent types, gold is responsible for many of their derivatives, commonly with a very restricted area of existence limited by this element. Within the former, gold is especially productive in the La_3Al_{11} branch, where certain types are not known with other element combinations. Some other types, i.e., ZrNiAl/Fe_2P, $YbMo_2Al_4$, and $MgCuAl_2$, take up gold as an ordinary member of the family, which can easily be substituted by a variety of other elements. A separate group of compounds includes some ternary phosphide/arsenide structures with redistribution of the elements. Gold occupies the position of phosphorus or another highly electronegative *p* element, while triels switch to the positions of transition metals. Since no other transition element reveals such behavior, the compounds are rather special antitype representatives and a bridge between phosphides and polar intermetallics. Finally, a small but distinct group of compounds (bottom of Table S6) contain the main characteristic feature of the family but cannot be completely described exclusively by this feature and are considered in more detail in section 6 of this Account. One compound from this group, $Na_{1.0}Au_{0.2}Ga_{1.8}$, deserves a bit more attention because of the almost uniform anionic tunnels augmented with cationic rings in a proportion of 3:1. The presence of a cation in the tunnel walls is quite unusual and serves as an extra confirmation of the stronger involvement of sodium in the covalent bonding.

3.4. Tunnels with Zigzag Chains of Counterions

In contrast to the three previous groups, certain compounds contain uniform straight or sinusoid-like tunnels with zigzag chains of cations. One big subgroup includes the orthorhombic branch of the AlB_2 type,[27] while others exhibit elements of variable-sized tunnels but with different stacking principles (Table S7). This collection of AlB_2 derivatives reveals significantly puckered single layers and a distribution of the interlayer contacts leading to distortion of the honeycombs and dislocation of the cations. The second subgroup contains a limited number of more complex structures with distinct motifs and more specific roles of gold. Among the ternary ordered representatives of the $BaZn_5$/$SrZn_5$ types, gold compounds

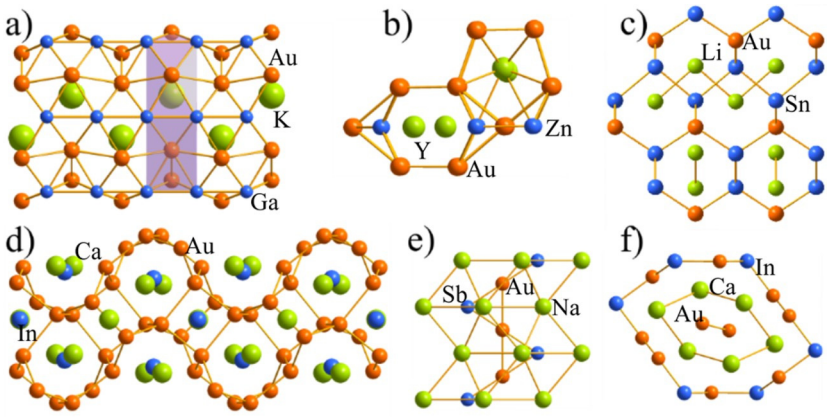


Figure 6. Zigzag chains in the crystal structures of (a) KAu_3Ga_2, (b) Y_3Au_5Zn, (c) Li_2AuSn_2, (d) $Ca_4Au_{10}In_3$, (e) Na_2AuSb, and (f) Ca_3Au_3In.

reveal preferred site occupations of the positions that are usually occupied by more electronegative elements, e.g., sulfur in KFe_2S_3. Such a site preference leads to the uniaxial distribution of Ga atoms in AAu_3Ga_2 with no dependence on the mutual tunnel orientation. The hexagonal rings forming the latter are shifted toward each other in the plane normal to the tunnel axis, forming a zigzag shape (Figure 6). The A_2AuPn series represents a kind of antitype for this structure with cationic hexagonal rings and Au/*Pn* zigzag chains. However, the pnictide positions are linearly distributed along the tunnel axis while Au atoms act as connecting links for them, forming the zigzag sequence $(AuPnAuPn)_n$. Similar but straight cationic tunnels with "encapsulated" polyanionic zigzag chains are observed in two compounds with the general formula $SrAu_{1-x}Cd_x$. The R_3Au_5Zn series instead contains straight uniform tunnels of puckered five- and six-membered rings of gold with an extra *p* element serving as a connecting link and leading to the zigzag shape of the cation chains within the hexagonal tunnels. The cation chain within the pentagonal channels exhibits just a minor deviation from the linear arrangement due to a uniform distribution of the Zn_2 pairs with respect to the former.

The ternary ordered representatives of the $Ni_{10}Zr_7$ and Ni_4B_3 types[30,31] exhibit a quite unusual involvement of anions in the tunnel centers. While it is not unusual that the Ni positions in $Ni_{10}Zr_7$ are substituted by Au, the position of Zr in the periodic table allows a wide variability of the elements filling its place. As a rule, these positions split for *s* and *p* elements, except for Mg, which can substitute a *p* element. Au atoms in these structures form sinusoid-like channels filled by cations and *p* elements in an alternating way. The latter build zigzag chains simultaneously in two directions with no direct cation−cation contacts in any of them. However, the chains are more uniformly distributed in the channels orthogonal to the gold waves. Ca_3Au_3In is another unique example with separate polyanionic and cationic channels. The main polyanionic network consists of 14-membered puckered rings surrounding smaller polycationic tunnels of puckered hexagons encapsulating gold zigzag chains. A similar situation is observed in Li_2AuSn_2, where Au and Sn atoms build a complex tetrahedral network as a result of mutually orthogonal zigzag chains, resulting in pseudohexagonal channels along the *a* and *b* directions. These channels in turn encapsulate zigzag chains of Li atoms.

4. MULTICENTERED POLYHEDRA

Perhaps the smallest collection of aurides that can be identified as a separate group on the basis of structural features is presented in Table S8. These compounds are, as a rule, gold-rich, and half of them have never been reported without gold, outlining the significance of relativistic effects in their stabilization. This group is partially related to the tunnel structures; however, cation groups within the tunnels are frequently separated by additional anions or the building blocks are twisted ($NaAu_4Ga_2$) such that the tunnels can hardly be observed. In contrast to the heavier alkali metals, Na in compounds with low sodium content prefers to form fused clusters. Each Na atom in such clusters does not exactly center its own polyhedron but shifts closer to the common center of the cation group (Figure 7). Since these clusters share big faces,

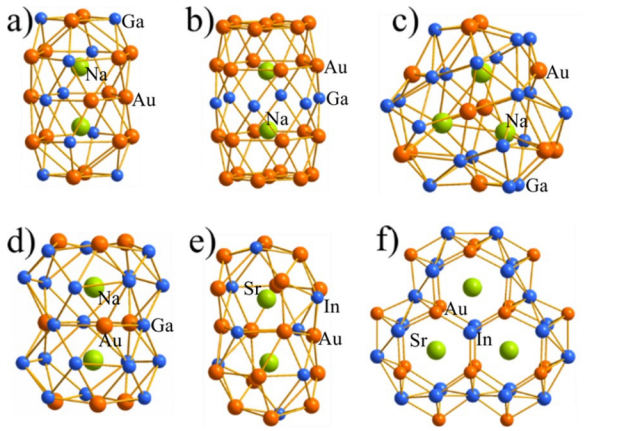


Figure 7. Multicentered polyhedra in (a, b) $Na_{13}Au_{41.2}Ga_{30.3}$, (c, d) $Na_5Au_{10}Ga_{16}$, (e) $NaAu_4Ga_2$, and (f) $Sr_2Au_3In_4$ and $Sr_4Au_9In_{13}$.

contain several cations, and are well-separated from the identical formations, they can be called multicentered polyhedra. The two compounds with strontium represent a slightly different, more regular modification in which the above-mentioned criteria combine with the open tunnels. $Gd_{14}Ag_{51}$-type compounds combine that structural motif with a bunch of others, as will be discussed in the next paragraphs.

5. STRUCTURES WITH TETRAHEDRAL MOTIFS

Tetrahedra are quite common in intermetallics, and they represent the main structural motif in Laves phases. In this

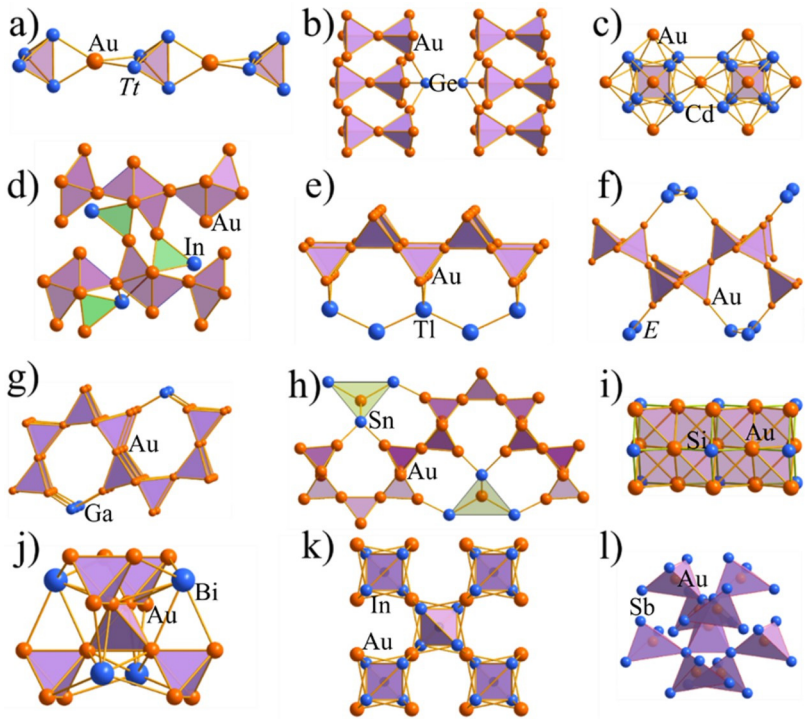


Figure 8. Tetrahedral motifs in the crystal structures of (a) A_3AuTt_4, (b) $A_4Au_7Ge_2$, (c) $Na_6Cd_{16}Au_7$, (d) $SrAu_{4.3}In_{1.7}$, (e) Rb_2Au_3Tl, (f) K_3Au_5E, (g) K_4Au_8Ga, (h) $K_{12}Au_{21}Sn_4$, (i) $CeAu_4Si_2$, (j) $CaAu_4Bi$, (k) Na_3AuIn_2, and (l) $R_3Au_3Sb_4$. All of the formal cations have been omitted for better clarity.

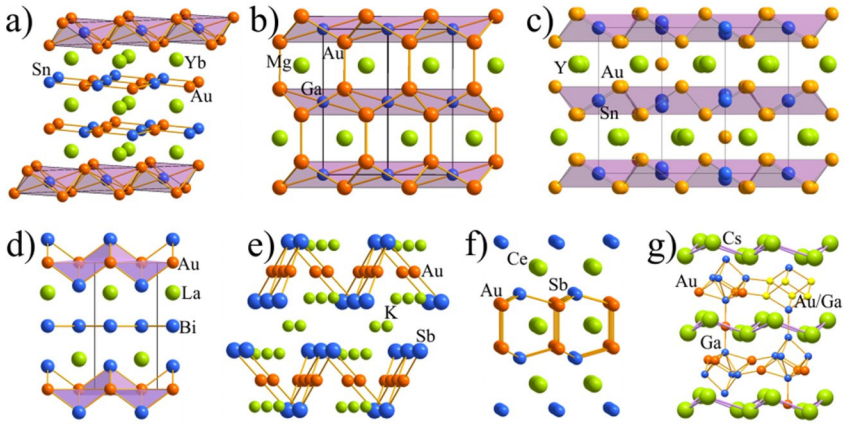


Figure 9. Characteristic fragments of the crystal structures of (a) $Yb_2Au_3Sn_2$, (b) $MgAu_2Ga$, (c) $Y_3Au_7Sn_3$, (d) $LaAuBi_2$, (e) $K_3Au_3Sb_2$, (f) $Ce_3Au_2Sb_3$, and (g) $CsAu_{1.4}Ga_{2.8}$.

section, we consider homoatomic Au tetrahedra, mixed formations, and the participation of Au in structures with tetrahedral formations of other elements, and we follow the formal role assignment within a given type. The general collection (Table S9 and Figure 8) can be divided into a few subgroups on the basis of the dimensionality of the tetrahedral motifs. A_3AuTt_4, $A_4Au_7Ge_2$, and $Na_6Cd_{16}Au_7$ represent formally isolated homoatomic clusters: Ge_4 tetrahedra, Au_7 vertex-sharing bitetrahedra, and Cd tetrahedral stars (TSs) connected to the neighboring identical units through additional heteroatoms. Rb_2Au_3Tl and $SrAu_{4.3}In_{1.7}$ instead exhibit 1D linear or zigzag chains of vertex-sharing Au tetrahedra. Au_4 tetrahedra in the former share two vertices with each other and are connected to the neighboring chains through zigzag Tl chains, while those in the latter form clusters of three face-sharing units with two common vertices within the chain and Au_3In tetrahedra between them. Wavelike 2D formations of vertex-sharing Au_4 tetrahedra have been observed in K_3Au_5E (E = Tl, In, Pb), K_4Au_8Ga, and $K_{12}Au_{21}Sn_4$. The difference within the group originates from diverse fragments separating them, which can be linear or zigzag p-element chains or even additional $Au@Sn_4$ tetrahedra. A slightly different situation is seen in two modifications of $CeAu_4Si_2$ where edge-sharing Au_4 tetrahedra form parallel slabs separated by additional Si and Ce atoms. Finally, real 3D structures are present in $CaAu_4Bi$, Na_2Au_3Al, Na_3AuIn_2, and $R_3Au_3Sb_4$. The homoatomic Au network in the first structure is reminiscent of the cubic Laves phase $MgCu_2$, while mixed but mostly ordered Au_3Al tetrahedra can be found in Na_2Au_3Al. Na_3AuIn_2 consists of mixed In-centered TSs. The latter structure is very complex despite its cubic symmetry and fairly small cell and is best

described as a 3D network of Au-centered vertex-sharing Sb_4 tetrahedra.

6. MULTICOMPONENT SYSTEMS

Many complex structures can be better described and understood in terms of simple intergrown layers or polyhedra. A decent number of aurides belong to this category. Except for the $CuHfSi_2$ and $Gd_{14}Ag_{51}$ types,[32,33] all of the structures in this group are either unique for gold or have a very restricted number of members in some cases (Table S10). The $CuHfSi_2$ type contains several hundred representatives and is not restricted solely to intermetallics. Its structure consists of three layers: *RE*, pnictide squares, and checkered up-and-down Au/*Pn* square pyramids with Au squares in the base. Similar structural motifs are also observed in $A_3Au_3Sb_2$, although with trigonal pyramids and only cationic layers separating them. The structure of $Ce_3Au_2Sb_3$ is instead best described as cationic planes sandwiched between puckered Au/Sb and planar Sb hexagonal layers. It contains two identical bigger fragments (three cationic planes per fragment) mutually shifted by $^1/_3$, $^1/_3$ in the *ab* plane, preventing the formation of tunnels along the *c* direction (Figure 9).

The next group of compounds contain cationic layers separated by more complex multilayer polyanionic formations. $MgAu_2Ga$ is formally isostructural with Na_3As and Mg_3Au, but with Ga in the position of the most electronegative element. Such a redistribution results in layers of edge-sharing $Ga@Au_6$ octahedra with maximal separation of Mg and Ga positions. Several modifications of this structural motif have been observed in a group of compounds including $Yb_2Au_3Sn_2$, $R_3Au_4Sn_3$, $R_5Au_8Sn_5$, $R_3Au_7Sn_3$, $R_2Au_5Sn_2$, and R_3Au_9Pn.[34] The three former compound series can be described with the general formula $R_{m+n}Au_{2m+n}Sn_{m+n}$ as an intergrowth of *m* GdPt$_2$Sn-type and *n* SrPtSb-type slabs.[35] The distribution of Sn atoms within the octahedra is planar, but the octahedral layers are separated by additional Au/Sn puckered hexagonal layers. The three latter series exhibit some alternation of Sn or *Pn* positions within the octahedral layers and, additionally, a few extra anions included in the cationic planes. Finally, two Cs−Au−Ga compounds exhibit an alternation of layers of puckered Cs hexagons and a polyanionic Au/Ga tetrahedral star network.

Following this tendency, obviously more complex cases of anionic slabs can be found in $LiAu_3Sn_4$ and two related structures of $Eu_5Au_{17.3}In_{4.7}$ and $Eu_5Au_{17.7}In_{4.3}$. While single planar cationic layers still exist in these structures, they represent a minor part of the structure and practically belong to a mixed slab. For example, the structure of $LiAu_3Sn_4$ consists of an anionic AuSn slab and mixed $LiAu_2Sn_2$ slabs of the NiAs and $CaAl_2Si_2$ types, while both Eu−Au−In compounds represent an intergrowth of two mixed $EuAu_2$ and $EuAu_{4+x}In_{2-x}$ slabs of $CeCu_2$ and $YbMo_2Al_4$ types. The situation in $K_{23}Au_{12}Sn_9$ is totally dominated by the cation because of the high concentration of the active metal in the compound. The $Au_{12}Sn_9$ anionic layer building blocks are fully separated by K atoms, with the latter being included also in the formally anionic slabs.

Six-membered "wheels" represent the three-component structure of $R_{14}(Au_{51-x}E_x)$ (E = *p* element). Irregular A1@M_{14} and A2@M_{14} polyhedra (Figure 10b) share tetragonal and trigonal faces, respectively, within a slab and trigonal faces between two different slabs, resulting in the "wheel axis" central $(A3)_2@M_{24}$ polyhedron. The latter was shortly considered above and is in fact a tunnel with five-membered rings

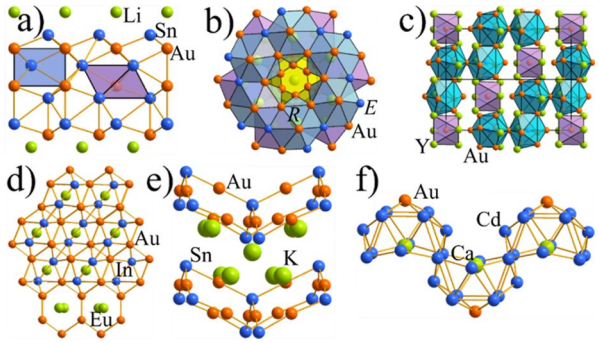


Figure 10. Characteristic structural motifs in (a) $LiAu_3Sn_4$, (b) $R_{14}(Au_{51-x}E_x)$, (c) Y_3Au_5Mn, (d) $Eu_5Au_{17}In_5$, (e) $K_{23}Au_{12}Sn_9$, and (f) $Ca_{11}Au_3Cd_{19}$.

according to 3/6/6/6/3. Similarly, no separate cationic or anionic layers are present in the crystal structure of R_3MnAu_5. This compound represents an intergrowth of $Au@R_6$ octahedra (in a ccp array) and $Mn@Au_8R_3$ polyhedra via edge and vertex sharing. The central part of the latter contains significantly distorted $Mn@Au_8$ cubes. A similar ccp arrangement of $R@Au_6$ octahedra has been observed in RAu_3Tr_7 phases with voids filled by Tr_7 clusters in the form of two tetrahedra with a common vertex. The same building principle has been observed in the complex phase $Ca_{11}Au_3Cd_{19}$, whose crystal structure can best be described as an intergrowth of mutually perpendicular zigzag chains of $Ca@(AuCd)_{15}$ half-polyhedra formally separated by additional Ca positions. $Na_2Au_6In_5$ is best characterized as the CsCl-type packing of $Au@In_{12}$ icosahedra and Au_6 octahedra surrounded by In cubes and $(In_2)_6$ octahedra. The last, but not the least, represented in this section are a family of Heusler phases[36] and the common intermetallics USi_2[37] and its derivative $ZrAl_2$[38] containing Au as an ordinary substituting element. The first is best described in terms of ZnS and NaCl structure types, while the latter can be characterized as an intergrowth of W and AlB_2 sublattices.

7. CONCLUDING REMARKS

In this Account, we have provided an overview of polar intermetallics with gold—a group of compounds that just has been systematically explored in the last few decades. Currently this group comprises several hundred representatives, while no attempts have been made to systematize their variety. We have analyzed the contribution of relativistic effects in the light of structural diversity in comparison with the isostructural or isocompositional nonrelativistic analogues.[16] Since the influence of relativistic effects in general and specifically in structural chemistry has been deeply investigated,[1,2] Pt and especially Au have been found to be the most exciting examples for their visualization. Besides the formation of truly ionic compounds with the heavy alkali metals,[4−9] their true nature is revealed through rather typical intermetallic compounds with atypical structural motifs, i.e., homoatomic networks (section 3.1), tetragonal tunnels with disordered counterions (section 3.2), and various homoatomic clusters (section 5). These are due to at least two factors: strong Au−Au bonding and the ability to form solid solutions with many other metals, especially *p* elements. Strong heteroatomic bonding with the latter instead allows for modification of the existing binaries and stabilization of new bonding schemes even with minor Au presence in the system.

Polar intermetallics with Au occupy relatively strict and narrow electronic ranges, a factor that is very important for the existence of many structural families. However, a separation of most subgroups on the basis of this criterion is hardly possible. Symmetry relationships have been found to be a good alternative criterion for immense systems such as intermetallics in general[21] and have partially been used for the arrangement of well-represented structural families with many derivatives. To prove/disprove the special role of Au in intermetallics, we have first applied the structural analysis at a rather macro level, considering polyhedra and their stacking, and then analyzed the importance of the presence of gold for the existence of a given ensemble. Five main differently populated groups could be outlined on the basis of (poly)anionic networks. Most of them reveal rather large subgroups existing solely with Au or, in some cases, containing a limited number of Pt or Ag members. Among such groups we would highlight homoatomic diamond-like Au networks, polytetrahedral networks or isolated clusters, uniform tetragonal tunnels with mostly disordered cations, and many more complex intergrown structures. Gold feels comfortable in any concentration range in a compound simply by changing its role from the main structure builder to complete mixing with other anions and, most interestingly, stabilization of new structures types with active metals. We believe that identifying these structural features opens considerable opportunities for alteration of the existing polar intermetallics with Au as well as the discovery of new compounds with the prospect of understanding of their structural−chemical−physical relationships to design new materials with desired properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.accounts.7b00316.

Ordered catalogue of all compounds considered in this Account (PDF)

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ACKNOWLEDGMENTS

This research was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract DE-AC02-07CH11358.

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